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Szabados Ágnes

Optimális szinteltoló paraméterek a perturbációszámításban

Eötvös Loránd Tudományegyetem,
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Doktori értekezésem az Eötvös Loránd Tudományegyetem Elméleti Kémia Tanszékén 1998 és 2001 között végzett munkám összefoglalása. Dolgozatom tárgya a nem időfüggő perturbációszámítás (PT) alkalmazása atomok és molekulák Schrödinger egyenletének közelítő megoldására.

Munkám során egy olyan általános elvet kerestem a Hamilton operátor nulladrendre és perturbációra osztására (az ún. perturbációs particionálásra), ami a PT alkalmazása szempontjából optimális. A perturbálatlan operátor diagonális mátrixelemeit módosító ún. szinteltoló paraméterekre egy variációs feltételt szabtam. Ez a feltétel a diagonális mátrixelemek egyértelmű felosztáshoz vezet, amit optimális particiónak neveztünk el. Az optimált particionálással mind az alacsony rendű korrekciókat, mind a PT sor konvergenciáját jobbnak találtam a hagyományos particióban számítottnál. Az optimált particiót az elektronkorreláció leírására alkalmazva, a másodrendű korrekció megegyezik az ún. Linearized Coupled Cluster Doubles, másnéven CEPA-0 közelítéssel.

Meghatároztam az optimális nevezőt a PT konstans denominátor közelítésében (Unsold-approximáció). Ennek a közelítésnek a PT kvázi-degenerált problémája kapcsán van jelentősége. Ezen kívül foglalkoztam a partició optimálásával egyszeres ionizáció perturbatív leírása esetén. E munka részeként egy levezetést adtam az időtől független Green függvényes módszer Dyson-egyenletére.

Ehelyütt szeretném köszönetem kifejezni a doktori munka során nyújtott segítségéért témavezetőmnek, Dr. Surján Péter egyetemi tanárnak.

Optimized level shifts in perturbation theory

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Introduction

Perturbation theory (PT) is a fundamental tool widely used in many areas of chemistry and physics to count for a little disturbance of a system that one has already described. The idea of PT is considerably old, it was first developed in connection with planetary motion in the XVIIIth century. The initiative was to describe the disturbance in the motion of planets, caused by the attraction arising between them, which is small if compared to the attraction between a planet and the Sun.

In some cases, like in that mentioned above, the physics of the problem provides a good basis for separating disturbance from the substantial effect. At other occasions (e.g. describing energetics of a many-electron system by PT) it may not be self-evident what is good to consider as perturbation. The choice of the unperturbed system is however a crucial question in PT, as the difficulties of its application (divergent series, quasi-degeneracy problem) in principle originate in an unfortunate choice for the zero order problem.

In any case where PT provides unsatisfactory corrections, there exists a possibility to modify the partitioning (the separation of the unperturbed system from the perturbation). A common way of doing so is to introduce so-called level shift parameters, that affect the division of the diagonal matrix elements between the zero order and the perturbation. The value of these parameters is in principle arbitrary.

In the thesis I address the question of finding a general rule for determining the value of the level-shift parameters. The results are summarized in the followings.

Determining an optimal partitioning

1. The level-shift parameters are obtained with the aid of the Rayleigh-quotient taken with the first order perturbed wavefunction. The condition for the shift parameters requires the stationarity of the above value, written up to O(3) (i.e. the energy up to third order).

2. A linear, inhomogeneous system of equations is got from the variational condition, determining the parameters that correcpond to those levels which interact with the ground state. Shifting the zero order eigenvalues with these parameters, a unique division of the diagonal elements is obtained. This division does not depend on the initial partitioning.

Refering to its variational character, the above partitionig is named "optimal partitioning". Some important

features of the optimal partitioning are collected in the following points.

3. The third order correction vanishes in the optimal partitioning. This results from that the condition for the optimal parameters is equivalent to setting the third order expression zero, term by term. In consequence, some terms of the higher order corrections also vanish.

4. The second order correction of the new partitioning may be obtained by a partial, infinite order resummation of certain (Brillouin-Wigner type) terms of the initial series.

5. Partitioning the diagonal elements in the optimal way preserves extensivity of the Rayleigh-Schrödinger PT. This is an important condition, not fulfilled in all approximative methods of quantum chemistry.

6. The optimal second order correction is invariant to a unitary transformation among the excited states interacting with the ground state, even if the zero order reduced resolvent is kept diagonal.

7. The so-called Epstein-Nesbet partitioning may be derived by considering a diagonal coefficient matrix in the system of equations determining the optimal level shifts.

8. The second order correction of the optimal partitioning may also be derived with the aid of Löwdin's partitioning technique. This derivation shows clearly the approximation steps leading from the exact eigenvalue to the optimal second order expression.

Applications of the optimal partitioning

The effect of repartitioning by the optimal level shift parameters has been tested in different applications of PT. In all the cases listed, low order PT corrections in the optimal partitioning are superior to the the standard partitioning. Computer codes have been written in FORTRAN 77.

9. On the example of a one-dimensional harmonic oscillator, perturbed by a quartic term, it is possible to solve analitically the system of equations determining the optimal shift parameters. Optimizing the partitioning extends the application of PT on this system for relatively large perturbations.

10. Using a Hartree-Fock determinant as reference state, the second order correction in the optimal partitioning as applied for describing electron correlation is identical with the so-called Linearized Coupled Clusters Doubles (LCCD), or CEPA-0 method.

11. In the case of describing electron correlation perturbatively, numerical studies have been performed to explore convergence properties of the PT series. Comparing the optimal partitioning with the Møller-Plesset partitioning, the former is found to converge faster.

12. The optimal parameter is determined in the constant denominator (Unsold) approximation of PT. The second order optimal correction within this approximation agrees with the second term of the so-called Connected Moment eXpansion (CMX). On a typical quasi-degenerate example (the symmetric dissociation of the water molecule) PT in the Unsold approximation, using the optimal denominator gives satisfactory results.

Describing single ionization by PT

Green's function or propagator methods provide a possibility to estimate energy differences (ionization and excitation energies) in a direct way. The central equation of these Green's function techniques is the Dyson equation of the Green operator, including the so-called self-energy operator, in a form of a PT series. The results of the thesis in this field can be collected in the points below.

13. A derivation of the Dyson equation of the time independent Green's function theory is presented. I believe that this derivation is more transparent than what one can find in the literature, and may help to understand better the essence of Greens' function or propagator methods as applied for estimating ionization/excitation energies.

14. A symple expression is obtained for the second order Dyson-correction of the ionization potential, that includes the matrix elements of the super perturbation operator. This is a simpler form than the one expressed with two-electron integrals, which may be of use if deriving higher order corrections.

15. Matrix elements of the super perturbation operator have been derived, that are needed for describing single ionizations perturbatively. The performance of the optimal partitioning has been tested in this application as well.

16. The so-called "shifted Born collision" approximation is obtained as an Epstein-Nesbet type partitioning based PT in this framework.

17. A second quantized like representation of superoperators is worked out to facilitate evaluating the effect of a superoperator on a product of second quantized operators. This makes it possible to consider substitution of second quantized operators instead of evaluating a commutator.

Publications

1. **Á. Szabados**, P. R. Surján: Optimized partitioning in Rayleigh-Schrodinger perturbation theory, *Chem. Phys. Letters*, **308**, 303 (1999).

2. P. R. Surján, **Á. Szabados**: Optimized partitioning in perturbation theory: comparison to related approaches, *J. Chem. Phys.*, **112**, 4438 (2000).

3. P. R. Surján, **Á. Szabados**: Constant Denominator Perturbative Schemes and the Partitioning Technique, *Int. J. Quant. Chem.*, in press

4. **Á. Szabados**, P. R. Surján: Optimized partitioning in PT: application for the equation of motion describing ionisation processes, *THEOCHEM.*, in press